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# SYNTHESIS OF HETEROCYCLIC ANALOGS OF CHALCONE CONTAINING THE SELENOPHENE RING

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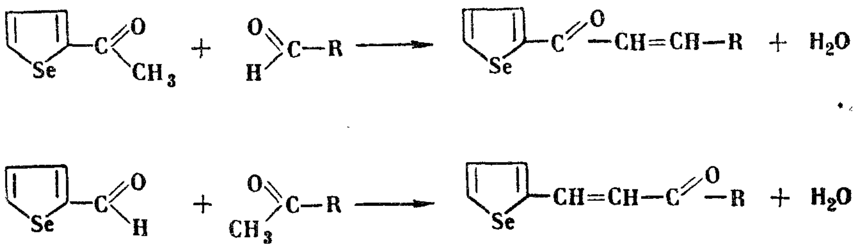
Crotonaldehyde-type condensation using alkaline or acid catalyst is used to synthesize 14 chalcone analogs containing in addition to the selenophene ring, a number of other heterocyclic groups. A Michael adduct is shown to be formed by reaction of 2-acetylselenophene with 2-pyridine aldehyde.

Synthesis of 1-(selenienyl-2)-3-arylpropenones containing electron-donating and electron-accepting substituents in the aromatic ring has previously been described [1]. In the present work it was decided to prepare chalcone analogs containing, in addition to the selenophene ring, one more heterocyclic group, viz. 2-selenienyl, 2-pyrryl, 2-furyl, 2-thienyl, 2-pyridyl, 2-quinolyl, 5-nitro-2-furyl, and 5-nitro-2-thienyl. There is nothing in the literature about such $\alpha,\beta$-unsaturated ketones, with the exception of 1-(selenienyl-2)-3-(thienyl-2) propenones which have been described by one of us with coworkers [2].

We have effected the synthesis of chalcone analogs containing the selenophene ring by crotonaldehyde-type condensation of 2-acetylselenophene or 2-selenophene aldehyde with the appropriate heterocyclic aldehyde or methyl ketones according to the equations:

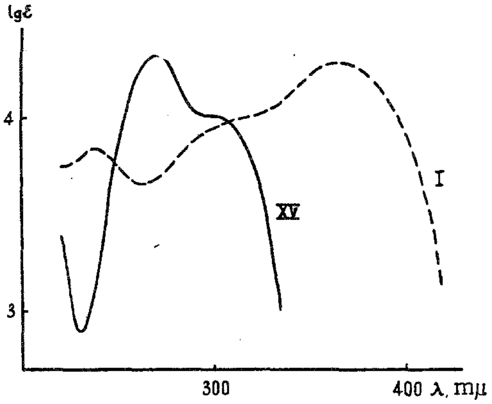


R = 2-selenienyl (I), 2-pyrryl (II, III), 2-furyl (IV, V), 2-thienyl (VI, VII), 2-pyridyl (VIII), 2-quinolyl (IX, X), 5-nitro-2-furyl (XI, XII), and 5-nitro-2-thienyl (XIII, XIV) (see table).

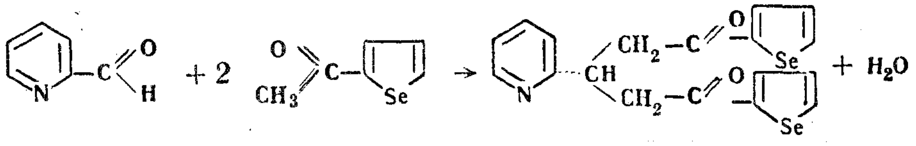
Ketones I-X are easily prepared by running the reaction at room temperature in aqueous ethanol, using an alkaline catalyst, 10% aqueous sodium hydroxide.

It should be mentioned that although synthesis of ketone VIII did not offer any difficulties, its isomer 1-(selenienyl-2)-3-(pyridyl-2) propen-1-one could not be obtained under the usual conditions, nor under the conditions which have been described for similar crotonaldehyde-type condensations involving 2-pyridine aldehyde [3]. In all cases only a negligible (4-8%) yield of the condensation product was isolated from 1 mole of 2-pyridine aldehyde and 2 moles of acetylselenophene (the Michael adduct), 1, 5-di(selenienyl-2)-3-(pyridyl-2) penta-1, 5-dione (XV).

The structure of this adduct is confirmed not only by its elementary analysis and that of its 2, 4-dinitrophenylhydrazone, but also by a study of its UV spectrum (see Fig.). The absorption curve is clearly different from that of heterocyclic chalcone analogs, and is characterized by an intense absorption band with $\lambda_{max}$ 270 mμ, characteristic of isolated carbonyl groups [4].



UV absorption spectra of ketones in ethanol: I) 1,3-di(selenienyl-2) propenone; XV) 1, 5-di(selenienyl-2)-3-(pyridyl-2) pental, 5-dione.



Heterocyclic Analogs of Chalcone Containing the Selenophene Ring, and Their 2, 4-Dinitrophenylhydrazones

| Ketone number | Ketone name | Mp, °C, external appearance | Formula | Se, % |  | 2, 4-Dinitrophenylhydrazones |  |  |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Found | Calc. | Mp, °C | λ max, mμ | Formula | Se, % |  |  |
|  |  |  |  |  |  |  |  |  | Found | Calc. |  |
| I* | 1, 3-Di (selenienyl-2) propenone | 104, Pale yellow needles | $C_{11}H_8OSe_2$ | 50.37;<br>50.05 | 50.28 | 256 | 440 | $C_{17}H_{12}N_4O_4Se_2$ | 31.77;<br>31.66 | 31.95 | 79 |
| II | 1-(Selenienyl-2)-3-(pyrryl-2) propen-1-one | 155, Orange parallelepipeds | $C_{11}H_9NOSe$ | 31.71;<br>31.72 | 31.56 | — | — | — | — | — | 66 |
| III | 1-(Selenienyl-2)-3-(pyrryl-propen-3-one | 155, Yellowish-green plates | $C_{11}H_9NOSe$ | 31.35;<br>31.50 | 31.56 | — | — | — | — | — | 55 |
| IV | 1-(Selenienyl-2)-3-(furyl-2) propen-1-one | 81, Pale yellow parallelepipeds | $C_{11}H_8O_2Se$ | 31.48;<br>31.37 | 31.44 | 249,5 | 428 | $C_{17}H_{12}N_4O_5Se$ | 18.01;<br>18.02 | 18.31 | 76 |
| V | 1-(Selenienyl-2)-3-(furyl-2) propen-3-one | 86, Pale yellow plates | $C_{11}H_8O_2Se$ | 31.35;<br>31.44 | 31.44 | 184 | 430 | $C_{17}H_{12}N_4O_5Se$ | 18.44;<br>18.30 | 18.31 | 92 |
| VI | 1-(Selenienyl-2)-3-(thienyl-2) propen-1-one** | 105, Pale yellow parallelepipeds | $C_{11}H_8OSSe$ | 29.57;<br>29.44 | 29.55 | 250 | 426 | $C_{17}H_{12}N_4O_4SSe$ | 17.80;<br>17.76 | 17.65 | 73 |
| VII | 1-(Selenienyl-2)-3-(thienyl-2) propen-3-one | 101, Pale yellow parallelepipeds | $C_{11}H_8OSSe$ | 29.74;<br>29.67 | 29.55 | 258 | 431 | $C_{17}H_{12}N_4O_4SSe$ | 17.44;<br>17.49 | 17.65 | 67 |

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* Ketones I-VII, IX and X were recrystallized from aqueous methanol, VIII from petrol ether, XI-XIV from acetic acid.

** There is a disturbing error in a paper by Yu. K. Yu'ev and his coworkers, [2]: 1-(selenienyl-2)-3(thienyl-2) propen-1-one in particular, melts at 105° (from petrol ether) and forms pale-yellow crystals; 1-(selenienyl-2)-3-(thienyl-2) propen-3-one melts at 100° (from petrol ether), yellow crystals. Absorption bands, characteristic of carbonyl groups, are present in the IR spectra: 1635 and 1640 $cm^{-1}$, corresponding bands for hydroxyl groups (3000-3600 $cm^{-1}$) were not found.

(table cont'd)

| Ketone number | Ketone name | Mp, °C, external appearance | Formula | Se, % |  | 2, 4-Dinitrophenylhydrazones |  |  |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  | Se, % |  |  |
|  |  |  |  | Found | Calc. | Mp, °C | $\lambda_{max}$, mμ | formula | Found | Calc. |  |
| VIII | 1-(Selenienyl-2)-3-(pyridyl-2) propen-3-one | 95,<br>Pale yellow parallelepipeds | $C_{12}H_9NOSe$ | 30.29;<br>30.16 | 30.11 | — | — | — | — | — | 73 |
| IX | 1-(Selenienyl-2)-3-(quinolyl-2) propen-1-one | 143,<br>Pale yellow plates | $C_{16}H_{11}NOSe$ | 25.16;<br>25.24 | 25.29 | 238 | 463 | $C_{22}H_{15}N_5O_4Se$ | 15.69;<br>15.67 | 16.04 | 85 |
| X | 1-(Selenienyl-2)-3-(quinolyl-2) propen-3-one | 128,<br>Pale yellow needles | $C_{16}H_{11}NOSe$ | 25.25;<br>25.03 | 25.29 | 213 | 451 | $C_{22}H_{15}N_5O_4Se$ | 15.79;<br>15.88 | 16.04 | 84 |
| XI | 1-(Selenienyl-2)-3-(5-nitrofuryl-2)propen-1-one | 170,<br>Pale yellow needles | $C_{11}H_7NO_4Se$ | 26.69;<br>26.73 | 26.66 | 252 | 454 | $C_{17}H_{11}N_5O_7Se$ | 16.27;<br>16.21 | 16.58 | 56 |
| XII | 1-(Selenienyl-2)-3-(5-nitrofuryl-2)propen-1-one | 188, 5<br>Yellow needles | $C_{11}H_7NO_4Se$ | 26.80;<br>26.75 | 26.66 | 203 | 436 | $C_{17}H_{11}N_5O_7Se$ | 16.15;<br>16.25 | 16.58 | 49 |
| XIII | 1-(Selenienyl-2)-3-(5-nitrothienyl-2)propen-1-one | 195,<br>Pale yellow plates | $C_{11}H_7NO_3SSe$ | 25.17;<br>25.44 | 25.29 | 224 | 446 | $C_{17}H_{11}N_5O_6SSe$ | 15.69;<br>15.75 | 16.04 | 58 |
| XIV | 1-(Selenienyl-2)-3-(5-nitrothienyl-2)propen-3-one | 179,<br>Yellow plates | $C_{11}H_7NO_3SSe$ | 25.45;<br>25.33 | 25.29 | 233 | 452 | $C_{17}H_{11}N_5O_6SSe$ | 15.83;<br>16.01 | 16.04 | 72 |

Regarding compounds XI-XIV, again it was previously shown that the starting intermediates 5-nitrofurfural, 5-nitro-2-acetylfuran, 5-nitro-2-thiophene aldehyde, and 5-nitro-2-acetylthiophene are readily resinified by alkali [5, 6], so that we carried out the synthesis of these ketones in glacial acetic acid, using concentrated sulfuric acid as the condensing catalyst. However, condensation products yields were considerably lower there, the reaction was complex and took 3-5 days, while the products were impure and had to be carefully purified.

All the heterocyclic chalcones which we have prepared are solids which crystallize well, soluble in ethanol, benzene (with the exceptions of XI-XIV), and acetic acid, but insoluble in water; VIII is unstable, and darkens on heating with ethanol.

Ketones I-XIV exhibit well-defined halochromic properties and in concentrated sulfuric acid—glacial acetic acid they deepen in color from yellowish-orange to reddish violet.

Ketones II, III, and VIII readily resinify with acids, and with the exception of these, all the ketones gave 2, 4-dinitrophenylhydrazones by the usual method[7]. The latter are characterized by their visible absorption maxima in chloroform solution as measured with a SF-2M spectrophotometer (see table).

## Experimental

The crotonaldehyde condensation in the presence of an alkaline catalyst was carried out in the way previously described [1].

Crotonaldehyde condensation in the presence of concentrated sulfuric acid. Stoichiometric quantities (0.01 mole) of the appropriate aldehyde and methylketone were dissolved in glacial acetic acid (10-15 ml), and the conc. $H_2SO_4$ (0.8-1 ml) added slowly, with stirring and cooling, when the reaction mixture gradually darkened. Reaction proceeded for some days (3-5). The black crystals which separated were filtered off, washed with ethanol, and recrystallized from acetic acid, using activated charcoal, till the melting point was constant.

1, 5-Di(selenienyl-2)-3-(pyridyl-2) penta-1, 5-dione (XV). A solution of equimolar amounts (0.01 mole) 2-acetylselenophene and 2-pyridyl aldehyde in 10 ml methanol was prepared, and 2 ml 10% sodium hydroxide dropped in, with stirring. Next day the crystals formed were filtered off, washed, and recrystallized from aqueous methanol. The white needle-shaped crystals had mp 122°, yield, 8%. Found: Se 36.32, 36.30%. Calculated for $C_{18}H_{15}NO_2Se_2$: Se 36.28%.

Bis-2, 4-dinitrophenylhydrazone. Dark red crystals mp 238°. Found: Se 19.91, 19.60%. Calculated for $C_{30}H_{23}N_9O_8Se_2$: Se 19.85%.

The UV absorption spectra of the ketones I and XV were determined in ethanol at concentrations of $2\text{-}3.5 \times 10^{-5}$ mole/l, using a SF-4 spectrophotometer.

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